PB83-116897

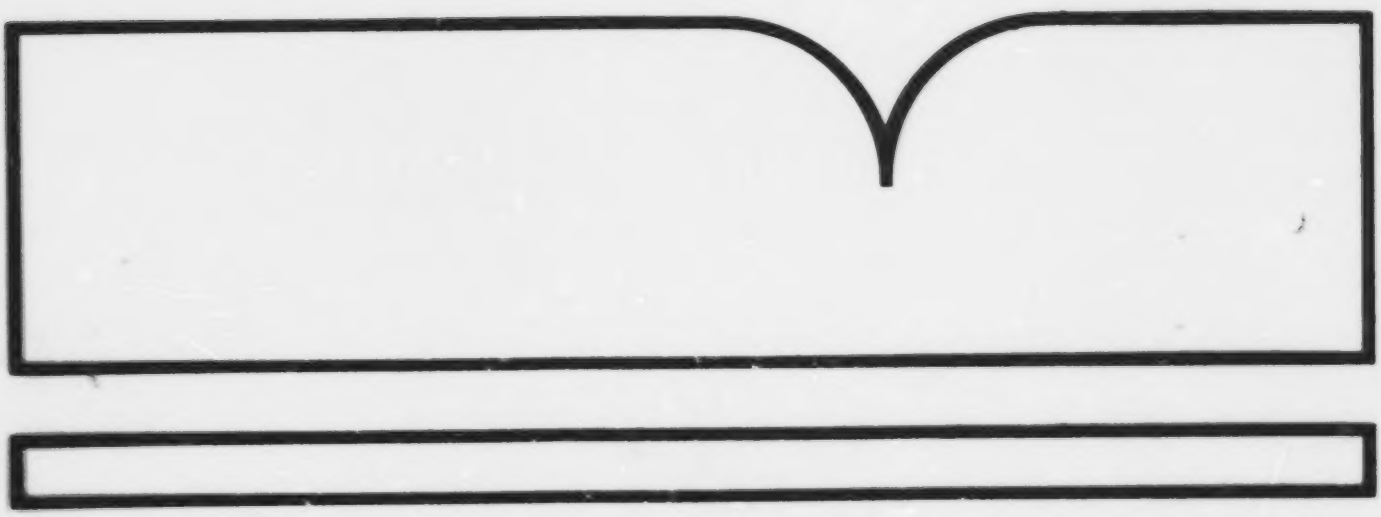
Organic Emissions from Iron Ore Sintering Plants: Determination of Causes and Methods of Abatement

Pittsburgh Univ., PA

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

Oct 82



U.S. Department of Commerce
National Technical Information Service
NTIS

PB83-116897

EPA-600/2-82-091
September 1982

ORGANIC EMISSIONS FROM IRON ORE SINTERING PLANTS

Determination of Causes and Methods of Abatement

by

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Grant Number R805304010

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Research Triangle Park, NC 27711

This study was conducted
under the co-sponsorship of
The American Iron and Steel Institute
Washington, D. C.

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-82-091		PB83-116897

4. TITLE AND SUBTITLE	5. REPORT DATE
Organic Emissions from Iron Ore Sintering Plants: Determination of Causes and Methods of Abatement	October 1982
	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Robert A. Stoehr	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
University of Pittsburgh Dept. of Metallurgical and Materials Engineering Pittsburgh, Pennsylvania 15261	11. CONTRACT/GRANT NO. EPA Grant R805304 (010)

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
EPA, Office of Research and Development* Industrial Environmental Research Laboratory Research Triangle Park, NC 27711	Final; 7/77 - 7/78
	14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Robert C. McCrillis, Mail Drop 63, 919/541-2733. (*) Cosponsor is the American Iron and Steel Institute.

16. ABSTRACT The report gives results of a laboratory study to develop basic information on the emission of organics from iron ore sinter beds. Samples of sinter bed mix components (including several types of iron ore fines, blast furnace flue dust, rolling mill scale, anthracite coal, and limestone) were obtained from three sinter producers. Small samples were heated in a tube furnace under a 100 ml/min flow of N2 or air. A combination of total organic analysis and full chromatographic analysis was used to determine the rate of organic emissions as a function of temperature and to characterize the nature of the emissions. Maximum emissions were observed between 300 and 500 C. Substantial emissions occurred as low as 100 C and as high as 800 C. They were less in air than in N2, indicating that combustion occurred even at comparatively low temperatures where the fixed carbon does not burn. Mill scale and blast furnace dust were shown to be the major sources of the organic emissions. These results suggest procedures for recycling the hydrocarbon-bearing gases through the hot sinter bed to produce complete combustion and for thermally pretreating the offending components.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Dust	Pollution Control	13B	11G
Sintering	Rolling Mills	Stationary Sources	13H	
Sintering Furnaces	Scale (Corrosion)		13I,13A	11M
Iron Ores	Anthracite Coal		08G	21D
Organic Compounds	Calcium Carbonates		07C	07B
Blast Furnaces			11F	

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	37
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (9-73)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

This laboratory project was initiated to develop basic information about the emission of organics from iron ore sinter beds. Samples of sinter mix and sinter mix components including several types of iron ore fines, blast furnace flue dust, rolling mill scale, anthracite coal, and limestone, were obtained from three sinter producers.

Small samples were heated in a tube furnace under a 100 ml/min flow of N_2 or air. A combination of total organic analysis and full chromatographic analysis was used to determine the rate of organic emissions as a function of temperature and to characterize the nature of the emissions. Maximum emissions were observed between 300°C and 500°C. Substantial emissions occurred as low as 100°C and as high as 800°C. They were less in air than in nitrogen indicating that combustion occurred even at comparatively low temperatures where the fixed carbon does not burn. Mill scale and blast furnace flue dust were shown to be the major sources of the organic emissions.

These results suggest procedures for recycling of the hydrocarbon bearing gases through the hot sinter bed to produce complete combustion and for thermally pretreating the offending components.

This project was completed by the University of Pittsburgh under joint sponsorship of the Environmental Protection Agency (Grant No. R805304010) and the American Iron and Steel Institute (Project No. 77-353). Work was performed between July 16, 1977, and July 15, 1978.

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ACKNOWLEDGEMENTS

The assistance of the American Iron and Steel Institute in co-sponsoring this project is hereby acknowledge. The project was initiated under AISI sponsorship in April, 1976 continued under joint sponsorship with EPA for the period covered in this report. Special thanks are given to Mr. Robert Fullerton of United States Steel Research Laboratories, Monroeville, Pa., for acting as project monitor for AISI and to those AISI member companies who provided samples of sinter mix components for our use.

The experimental program was carried out by Mr. Jerome W. Osheka, graduate student researcher, and Miss Denise Wanamaker, undergraduate student assistant, in partial fulfillment of the requirements for the degrees of Master of Science and Bachelor of Science, respectively, at the University of Pittsburgh.

SECTION 1

INTRODUCTION

The objective of this project is to develop basic information about the conditions under which hydrocarbons* are emitted from iron ore sinter beds and to investigate techniques for their elimination at the source.

Iron ore sintering is an essential operation for the steel industry. It is one of the principal methods for agglomerating iron ore fines into a feed material suitable for the blast furnace. Furthermore, it is unique among agglomerating methods in that it permits the recycling of certain waste materials which are high in iron value and fuel value. These include rolling mill scale and blast furnace flue dust and filter cake (1). Without such a method, not only would the values in these materials be lost, but disposing of them would present an additional problem. Iron ore fines, iron ore concentrates, coke, coke breeze, anthracite coal, and limestone are used in various proportions to complete the mix (1,2). Typically, 5 per cent of the mix is combustibles (3).

The materials are blended, mixed with a controlled amount of moisture, agglomerated on a balling drum or disc, then fed onto the travelling grate of a downdraft sintering machine. The material is ignited from the top. Suction in the windboxes pulls air down through the bed. The ignited layer, or "flame front", moves downward through the bed as the bed moves along the machine on the travelling grate (4). The temperature rises to about 1315°C to 1485°C as the flame front passes (5,6). The flame front reaches the bottom of the bed just before the bed reaches the discharge end of the line. Conditions below the flame front are reducing, while in the cooling bed above the flame front, oxidizing conditions prevail.

Hydrocarbons enter the sinter mix with a number of the components; principally with blast furnace flue dust and filter cake, and oil-coated mill scale. Many of the hydrocarbons leave the bed unburned or partially burned and enter the wind boxes. They are volatilized in the preheating zone below the flame front where the conditions are reducing and so they do not burn or they burn incompletely. Temperatures are not high enough in the wind boxes to insure burning of the hydrocarbons after they leave the bed (5).

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* The term "hydrocarbon emissions" as used in this report should not be interpreted as referring to compounds containing only hydrogen and carbon. It refers, instead, to the broader classification commonly called organics which encompasses those compounds containing other elements in addition to hydrogen and carbon as well as those containing only hydrogen and carbon.

The hydrocarbons emitted from the bed may be subsequently condensed or allowed to escape into the atmosphere. When they condense in the pollution control system, they seriously interfere with the operation of the dust removal equipment. They produce gummy deposits on filter bags which tend to blind the bags (7). They cause fire hazards in electrostatic precipitators. They are sometimes handled with high-energy wet scrubbers or wet electrostatic precipitators, but they make the water treatment from such systems more difficult (8). If they are released to the atmosphere they may put the operation in violation of air pollution control regulations on the basis of visible plume or on the basis of excess particulates when the weight of the condensable hydrocarbons is added to the weight of the solid particulates.

Efforts to control hydrocarbon emissions by control of the sintering process have involved control of sinter mix composition, moisture content, bed permeability, and air flow rates. Pretreatment of certain components to remove the hydrocarbons before blending them into the sinter mix is possible, but it involves additional operating costs. In addition, recycling the off-gas from the windboxes with the highest hydrocarbon content back through the bed on another part of the line has been proposed. This would cause the hydrocarbons to pass through the high temperatures and oxidizing conditions existing in the flame front. It has met with partial success where it has been tried in industry, and it involves substantial capital investment. (9,10)

The experiments performed in this project have been designed to obtain basic information on the conditions under which hydrocarbons are emitted from sinter bed materials to aid in the control of the process and the design of systems for improved pretreatment of components and recycling of the off-gas.

This project was begun in May, 1976, under the sponsorship of the American Iron and Steel Institute (AISI) and continued after July, 1977, under joint AISI - EPA sponsorship.

SECTION 2

CONCLUSIONS

Mill scale and blast furnace flue dust are the major sources of organic emissions from sinter beds.

The range of temperatures over which substantial emissions occur varies with the producer and the components used in the mix. It may extend from 100°C to nearly 800°C.

Higher oxygen potentials result in lower hydrocarbon emission rates. Combustion of some of the hydrocarbons occurs, even though the temperatures are too low for ignition of the fixed carbon.

The full chromatographic analyses reveal that the emissions are predominantly of low molecular weight, indicating that thermal decomposition is occurring. This effect becomes more pronounced at higher temperatures. The percentage reduction of emissions in air is much greater in the complete sinter mix than the individual components. The greater reductions achieved on the complete mix probably indicate that the oxidation of hydrocarbons at these temperatures requires a surface, and that the iron oxides and other materials, which are more prevalent in the complete mix, provide such a surface.

After sinter mix components have been heated to 700°C in nitrogen, they are free of volatile hydrocarbons but the fixed carbon remains.

The data obtained on this project are of significance in the redesign of sinter lines in the following ways. They define the range of temperatures over which sinter bed materials actually emit organic vapors. They show which materials produce the most emissions. They show that thermal pretreatment of the offending components could effectively remove the hydrocarbons while leaving the fixed carbon. They show that substantial diminution of the emissions can be achieved by oxidation if the oxygen potential is kept high as it is in air, and that the presence of materials found in sinter mix appears to aid this oxidation, presumably because they contribute surfaces where oxidation can occur. The full chromatographic analyses show that a much higher percentage of the emissions than previously suspected may be in the form of low molecular weight hydrocarbons. Furthermore, the analytical procedures developed for this project could be applied to monitoring hydrocarbon emissions on industrial sinter lines.

SECTION 3

RECOMMENDATIONS

Further study is needed to establish the optimum conditions for recycling gases through the sinter bed to eliminate hydrocarbon emissions. Laboratory tests should be made on a model sinter bed system, using the analytical procedures described in this report. They should determine the exact point in the sintering cycle when emissions are the heaviest and the best point on the sinter line for feeding these emissions back through the bed to burn them completely. Field studies should be used to verify this information on production sinter lines. Based on this information, effective recycle systems should be developed to eliminate the hydrocarbon emission problem.

Thermal pretreatment has been shown to be an effective method of removing hydrocarbons while leaving the fixed carbon in the sinter mix components. Further study is needed to demonstrate that a mix made from such components will sinter properly and make a good product. Furthermore, it must be demonstrated that pretreatment could be done with waste heat from the process to make it economically feasible.

The relationship between metallurgical process operating variables and hydrocarbon emissions should be studied for other processes. High priority should be given to the study of non-ferrous roaster operations which use acid plants to control SO_2 emissions. Flotation oils on the ore concentrates can produce unburned hydrocarbons in the flue gas which cause the acid to turn black. This seriously upsets the economics of operating this type of air pollution control equipment.

SECTION 4

MATERIALS

Sinter mix samples were obtained from three major producers of iron ore sinter: Bethlehem Steel Corporation, Jones and Laughlin Steel Corporation, and United States Steel Corporation. Samples were shipped to us in sealed cans. In addition to samples of the complete mix, samples of the sinter mix components were supplied to us by the producers. These components included rolling mill scale, blast furnace flue dust, Quebec ore concentrate, Mesabi ore fines, Venezuela fines, calcine, black sand, and anthracite coal.

It is not the purpose of this project to make comparisons between the producers of these materials and so the results are identified as being from Producer A, B, or C rather than by company name.

SECTION 5

EXPERIMENTAL PROCEDURES

GENERAL PROCEDURES

The samples of sinter materials were thoroughly blended and subdivided into specimens of 3.0 to 10.0 g for performance the test procedures described below.

The general procedure was to place the specimen on a porous support in a vertical combustion tube, heat it at a prescribed rate while passing a controlled atmosphere through it, and analyze the effluent gases for hydrocarbons using a gas chromatograph with a flame ionization detector.

From the beginning, it was realized that the emissions should be analyzed continuously so that the total quantity of hydrocarbons emitted could be determined. This proved to be impossible when the GC was used in the conventional manner, because long times (near 1 hour) were needed to provide good separation between the hydrocarbons from C1 to C24.

Several techniques were used in efforts to overcome this problem before a truly effective procedure was developed. The early techniques included capturing the off-gas in gas sampling bottles which were stored until they could be analyzed, absorbing the hydrocarbons in hexane or benzene for later analysis, capturing the hydrocarbons by condensation at liquid nitrogen temperatures, and measuring emissions by measuring weight loss as the specimen is heated. These techniques and the problems that arose with them are described briefly in the following section on Preliminary Test Techniques.

A technique was then devised utilizing a combination of total hydrocarbon analysis, which could be performed on a nearly continuous basis, and full chromatgraphic analysis, which could be performed at selected temperatures. This technique is described in the section on The Combination Analytical Technique.

A 7.5-cm dia model sinter bed was built and tested. It was demonstrated that this unit could burn sinter, but it was not used with analytical equipment described in this report.

Preliminary Test Techniques

The sample of sinter bed material was placed in a 1-in dia mullite tube and the gas flow started at 200 ml/min. The temperature was raised quickly to a predetermined temperature. Gas samples were collected alternately in a 250-mℓ gas sample bottle and by absorption in chromatographic grade benzene

at 0°C. The specimen was then raised quickly to the next test temperature, and another gas sample was collected. Samples were drawn from the gas sample bottles or benzene absorption impingers by hypodermic syringe for transfer to the GC.

Initally, it was planned to take samples at 25°C increments at about 15 minute intervals. It was found, however, that because the samples contained hydrocarbons in a wide range of molecular weights, long run times and temperature programming of the chromatograph were necessary. The actual GC analysis time was 30 min with a starting temperature of 50°C and a final temperature of 275°C. The column then had to be cooled back to 50°C and equilibrated before the next specimen could be injected. This resulted in an overall time between injections of 1 1/2 hours and explained why it was impossible to adhere to a schedule calling for the taking of a sample every 15 minutes. Tests showed that samples of this type could not be stored for long periods in the sampling equipment available. Therefore, much larger temperature intervals were used. Usually 100°C, 400°C, and 800°C were used on each specimen.

These discontinuous tests produced some information. Specifically, they showed that blast furnace flue dust was the most concentrated source of hydrocarbon emissions, and that mill scale was second. They also showed that the greatest evolution occurred at bed temperatures between 300 and 400°C with the lower limit about 100°C and the upper limit about 800°C. Hydrocarbons around C6 to C8 predominated, but smaller quantities out to C20 were observed. The weight loss tests showed the greatest losses between 75 and 300°C.

A series of tests were run which clearly showed that syringe sampling introduced a great deal of variability into our analytical procedures. Various methods were tried for capturing and preserving the hydrocarbon vapors but none gave stable, reproducible results. These methods included capturing the sample in heated 250-ml gas sampling bottles. Even when heated to 200°C, the heavier hydrocarbons were lost with time, presumably by condensation. The solvent absorption methods were unsatisfactory because they did not capture the lighter hydrocarbons and because the solvents such as hexane or benzene gave GC peaks right where we were most interested in seeing the emissions from the sinter materials.

Cryogenic capture of the hydrocarbons in a cold trap cooled by liquid nitrogen and by a dry ice-alcohol mixture did not work. The condensation of water tended to block the cold trap and the whole thing was messy.

Thermal arrest measurements and thermal gravimetric measurements were also tried, but these ran into serious interference due to moisture evolution from the specimen.

The Combination Analytical Technique

The eventual apparatus for testing sinter mix components is shown in Figure 1. A 3.0 gram sample is placed in a vertical 13-mm dia silica glass tube (C). A fritted silica disc provides support for the sample. The tube is heated in a resistance wound tube furnace (B). A thermocouple inserted directly into the sample measures the sample temperature independently of the

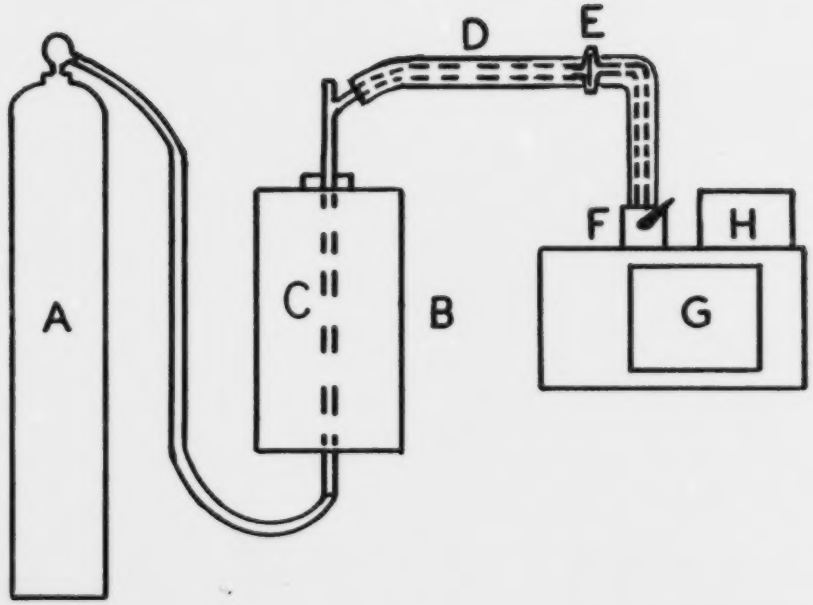


Figure 1. Sinter Mix Component Apparatus.

a. Gas Supply
b. Tube Heating Furnace
c. 13-mm Vycor Sample Tube with Fritted Disc
d. Heated Line
e. Filter
f. 8-port Sample Valve
g. Cas Chromatograph Column
h. Flame Ionization Detector

furnace temperature.

The sample heating tube is connected to the GC through a 3.17-mm (0.125-in) dia heated stainless steel line (D). A heated glass fiber filter (E) is located in the line to remove particulates. The eight-port gas sampling valve (F) is located in a heated compartment on top of the GC. Each time the sample valve is actuated, a 1-ml gas sample is injected into the chromatograph. This sample valve results in much less variability than the hypodermic syringes used previously.

A 3.0 gram sinter mix sample size has been chosen because this allows all of the off-gas to go through the sample line and valve without overloading the flame ionization detector in the GC. The gas flow rate has been standardized at 100 ml/min.

In order to perform total hydrocarbon analysis, a short column (25.4-cm or 10-in long) of SP 2100 on 80/100 Supelcoport* is used at a constant oven temperature of 250°C. This causes all of the hydrocarbons to be eluted to the flame ionization detector (FID) in a single peak. The FID responds specifically to organic carbon. Our tests have verified that other carbon such as CO_2 does not interfere. Because only one peak need be observed, sample repetition times can be as short as 15 sec.

Gas samples are collected in the same way for total hydrocarbon analysis as for full chromatographic analysis. The difference lies in the choice of the column and its temperature of operation.

For full chromatographic separation of the hydrocarbons a 6-ft long column of SP 2100 on 80/100 Supelcoport is used. The column oven temperature is programmed, starting at 50°C and heating at 10°C per minute to a final temperature of 250°C. This produces a separation of the hydrocarbons from C1 to C24, but it takes more than one hour from sample to sample when the oven cooling time is also considered. Table 1 contains a list of the mean values of retention times we have obtained on our calibration runs for the normal paraffins from C1 to C24. Note that C1 and C2 are eluted as a single peak. Table 1 also contains additional information on the conditions used in all of our full chromatographic analyses.

A standard mixture of 100 ppm hexane in nitrogen is the primary calibration standard. A mixed calibration gas containing 100 ppm of the n-paraffins from C1 to C6, and liquid calibration mixtures of the n-paraffins from C7 to C24 are also available.

With our equipment, total hydrocarbon analysis and full chromatographic analysis cannot be done at the same time. When both analyses are wanted on the same material, duplicate samples must be prepared. Total hydrocarbon analysis is done first. Then a duplicate sample is heated under the same conditions, and a full chromatographic separation is performed on a gas sample

*Trademarks of Supelco, Inc., Bellefonte, Pa., for a methyl silicone fluid phase on an acid washed DMCS treated diatomite support. Trademarks included for identification purposes and do not constitute an endorsement.

Table 1
Calibrated Retention Times
of n-Paraffins

RT (minutes)*	n-Paraffin
0.61	C1 and C2
0.62	C3
0.82	C4
1.18	C5
2.03	C6
3.11	C7
5.14	C8
7.14	C9
8.98	C10
12.18	C12
15.00	C14
17.52	C16
19.72	C18
20.79	C20
23.87	C22
27.03	C24

*Retention times calibrated for the following conditions.

Column: 1/8" dia-6 ft long SP 2100 on 80/100 Supelcoport

Carrier Gas: N_2 Flow: 20 cc/min

Initial Temp: 50°C Time at Initial Temp: 2 min.

Heating Rate: 10°C/min Max Temp: 250°C

Injection Temp: 165°C FID Temp: 300°C

These conditions were used for all chromatographic analyses contained in this report.

drawn at some point on the heating curve. We chose to run full chromatographic analyses at the temperatures where peaks and valleys were observed on the total hydrocarbon curve. We also ran analyses at the temperature on the lower side of the first peak where emissions equal one-half of the emissions at the first peak, and at the temperature on the upper side of the highest peak where emissions equal one-half of the emissions at the highest temperature peak.

SECTION 6

RESULTS AND DISCUSSION

The fast repetition rate of the total hydrocarbon technique allows the development of profiles of emissions as a function of time and temperature. Figure 2 is a reproduction of the trace of hydrocarbon analyses in the raw form made by the chromatograph. The chromatograph automatically prints the time when each peak is detected. It also calculates the area of each peak. The area is a better measure than the peak height of the quantity of hydrocarbon detected. In Figure 3, the concentration of total hydrocarbons in the effluent gas, based on peak areas, is plotted in bar graph form. In Figure 4, this same information has been plotted as a function of sample temperature.

Figures 5 through 11 show the hydrocarbon emissions as a function of temperature for sinter mix components obtained from three different producers. Each curve is, in effect, the envelope which would enclose the bar graph of the type shown in Figure 4. The two curves on each figure show the reproducibility of the results obtained from two samples of the same mix.

In Figures 5 through 11, the scale for plotting the hydrocarbon emissions is $(mg/m^3)/g$. This refers to milligrams of hydrocarbon per cubic meter of gas per gram of sample. The proper units of concentration for air pollutants are micrograms of pollutant per cubic meter of atmosphere. Milligrams have been used on these figures instead of micrograms, because the observed values can be expressed as smaller numbers. Our primary calibration standard is 100 ppm of hexane in nitrogen. For hexane, mg/m^3 can be converted to ppm by dividing by 3.58. This conversion is applicable to hexane only. For hydrocarbons in general, the conversion is done by dividing by (307.9/M.W.). The gas flow rate through the tube containing the sinter material was 100 cc/min and the sample of sinter bed material was initially 3.0 g in all cases.

Figure 5 shows the emissions obtained from sinter mix obtained from producer's plant A. It shows that the emissions reach a maximum value of 150 $(mg/m^3)/g$ at 496°C in nitrogen and that the temperatures over which substantial emissions occur range from 300°C to 700°C. It also shows that the emissions are considerably less when heated in air, reaching a maximum of 25 $(mg/m^3)/g$ at 276°C. Burning of the hydrocarbons apparently occurs as the temperature increases above that point because of the higher oxygen potential of the air.

Figure 6 shows the emissions from the sinter mix obtained from producer's plant B. The emissions show two peak temperatures, both in nitrogen and in air. The maximum values of the emissions are lower from plant B than from plant A, but they extend over a wider range of temperatures, beginning around 100°C and extending to around 800°C.

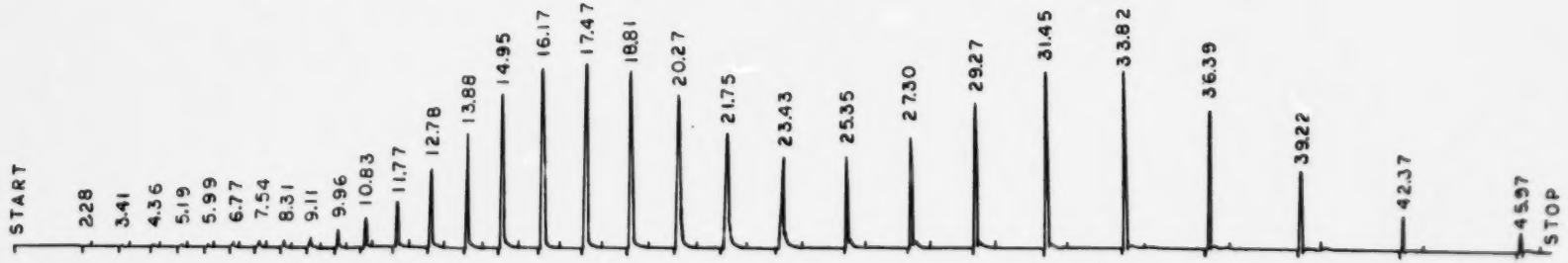


Figure 2. Total Hydrocarbon Trace in Raw Form Produced by Chromatograph. Numbers above peaks represent time in minutes after start of run. Times are then correlated with sample temperatures to produce the representation of the type shown in Figure 3.

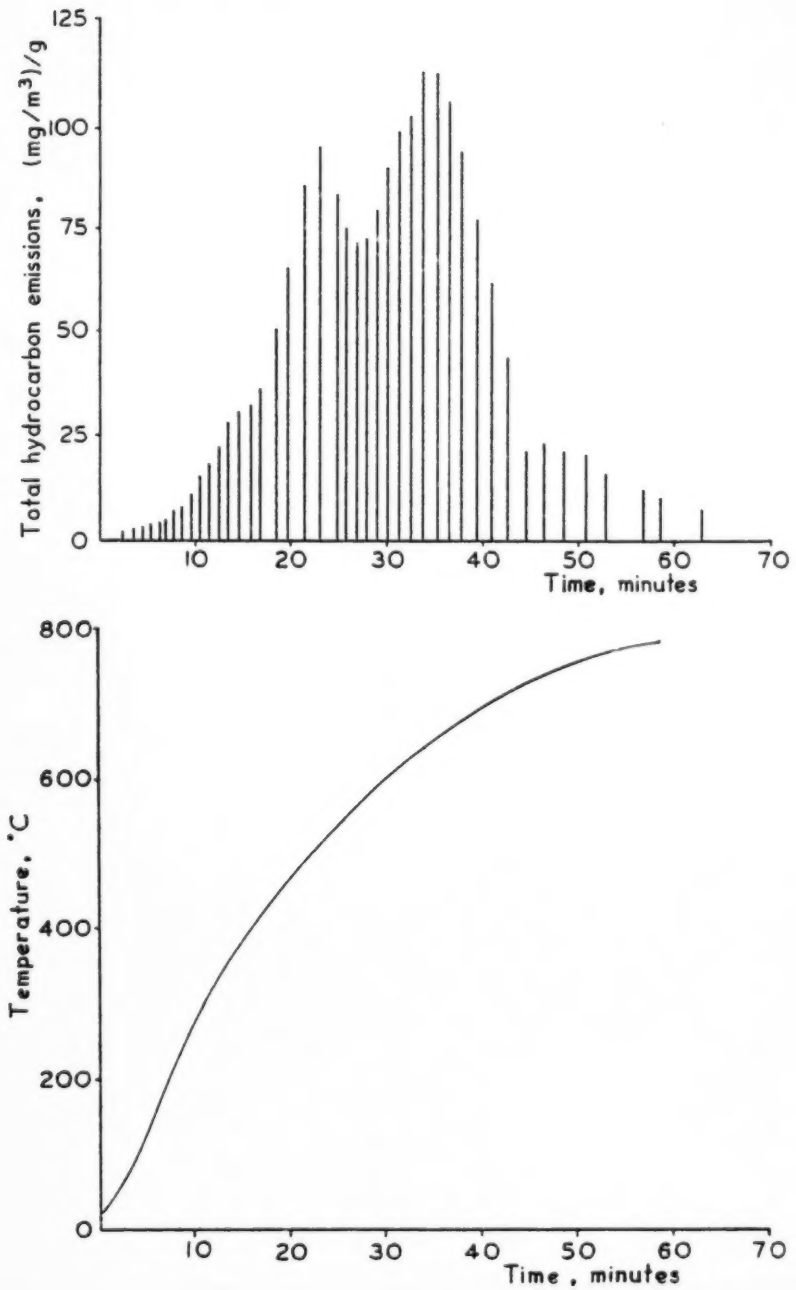


Figure 3. Total Hydrocarbon Emissions as a Function of Time (Top). Sample Temperature as a Function of Time (Bottom).

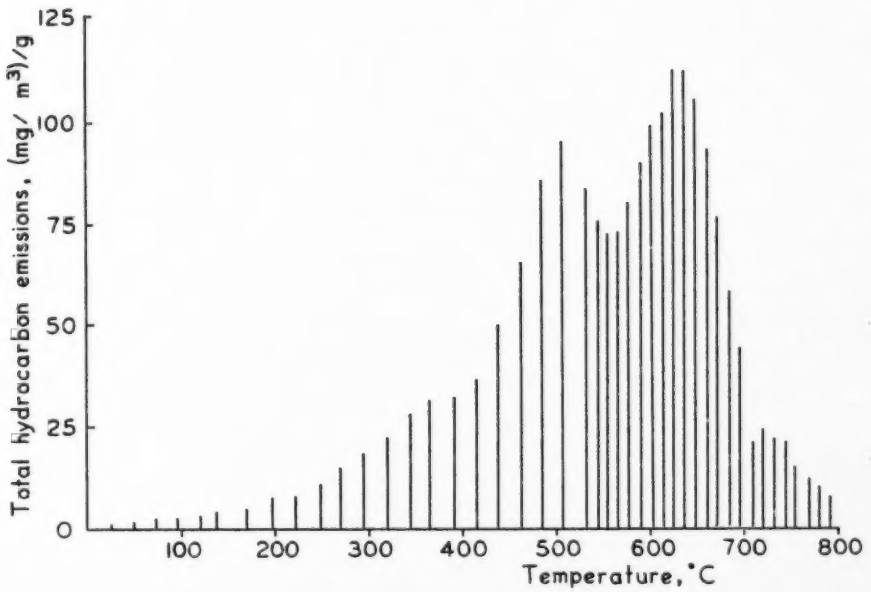


Figure 4. Total Hydrocarbon Emissions as a Function of Sample Temperature in Bar Graph Form.

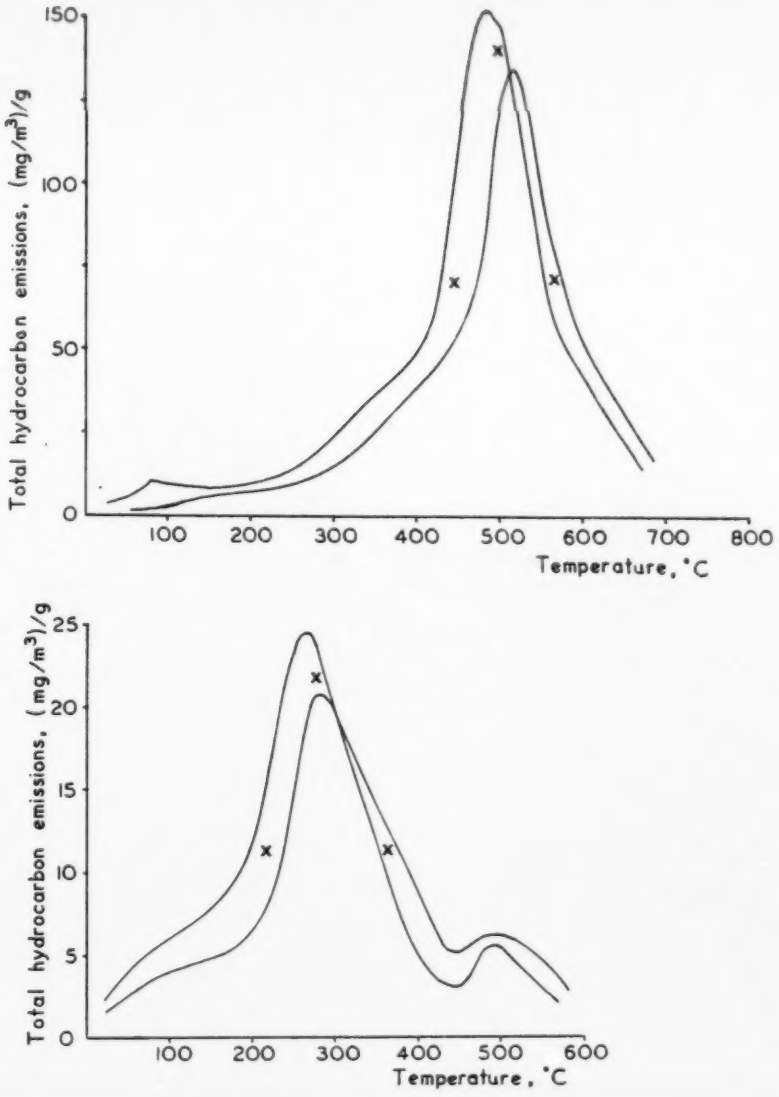


Figure 5. Total Hydrocarbon Emissions. Complete Sinter Mix - Plant A
Top - Heated in Nitrogen. Bottom - Heated in Air.
X Indicates Sample Taken for Full Chromatographic Analysis.

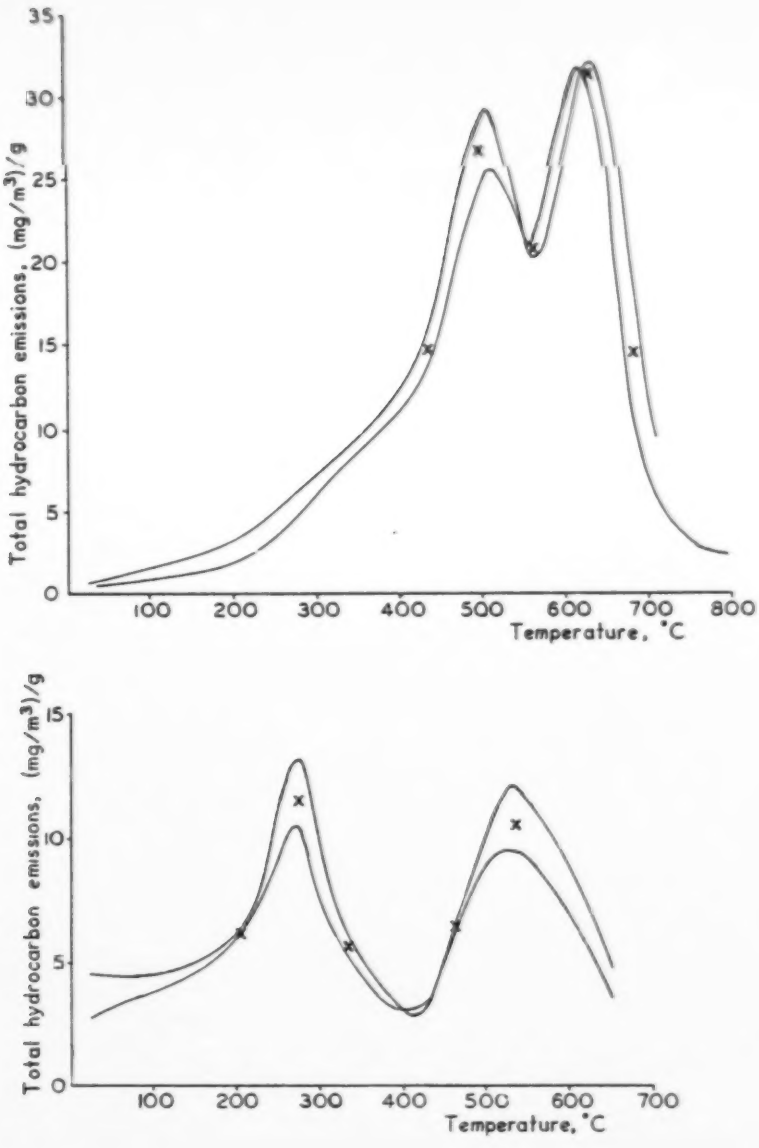


Figure 6. Total Hydrocarbon Emissions. Complete Sinter Mix - Plant B. Top - Heated in Nitrogen. Bottom - Heated in Air. X Indicates Sample Taken for Full Chromatographic Analysis.

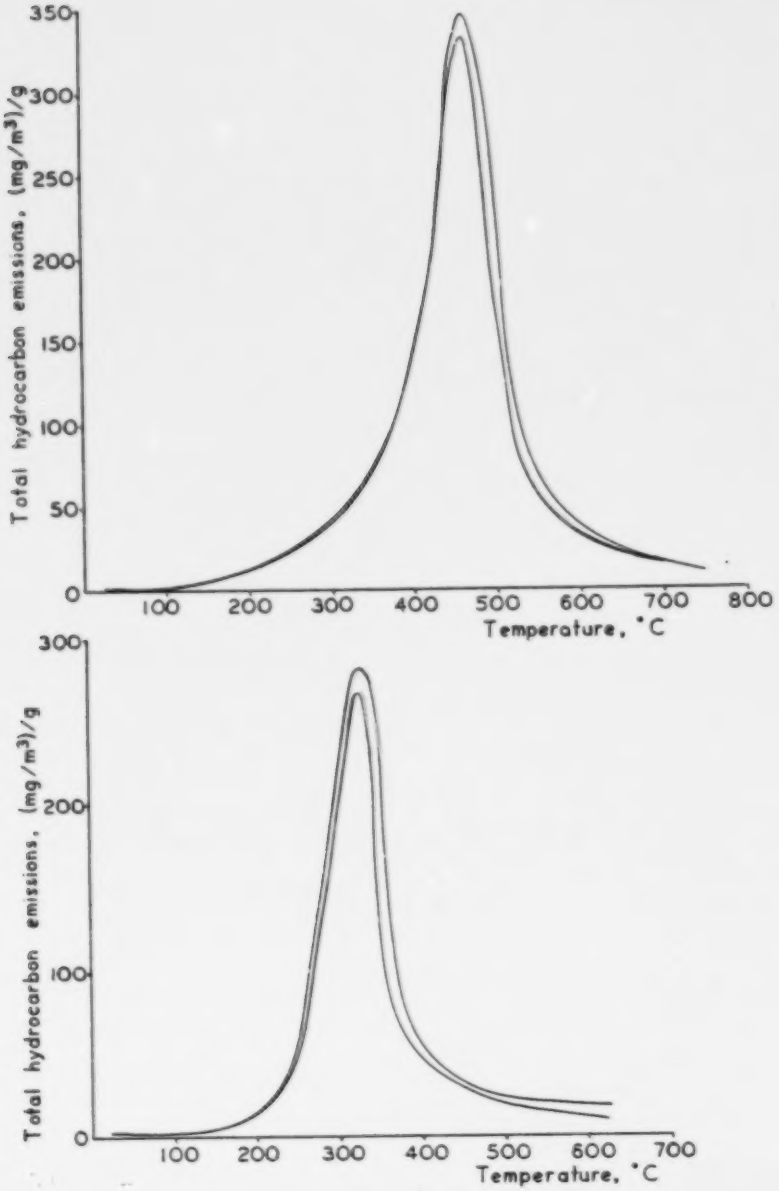


Figure 7. Total Hydrocarbon Emissions. Mill Scale - Plant A. Top - Heated in Nitrogen. Bottom - Heated in Air.

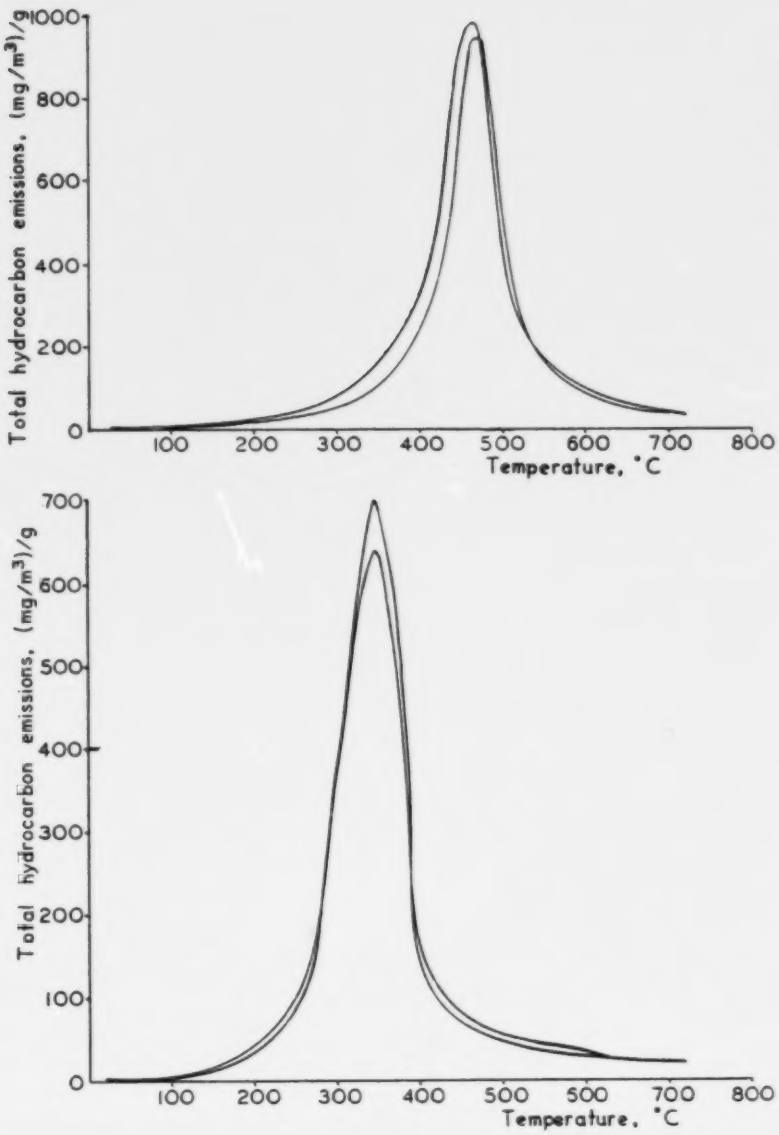


Figure 8. Total Hydrocarbon Emissions. Mill Scale - Plant B.
Top - Heated in Nitrogen. Bottom - Heated in Air.

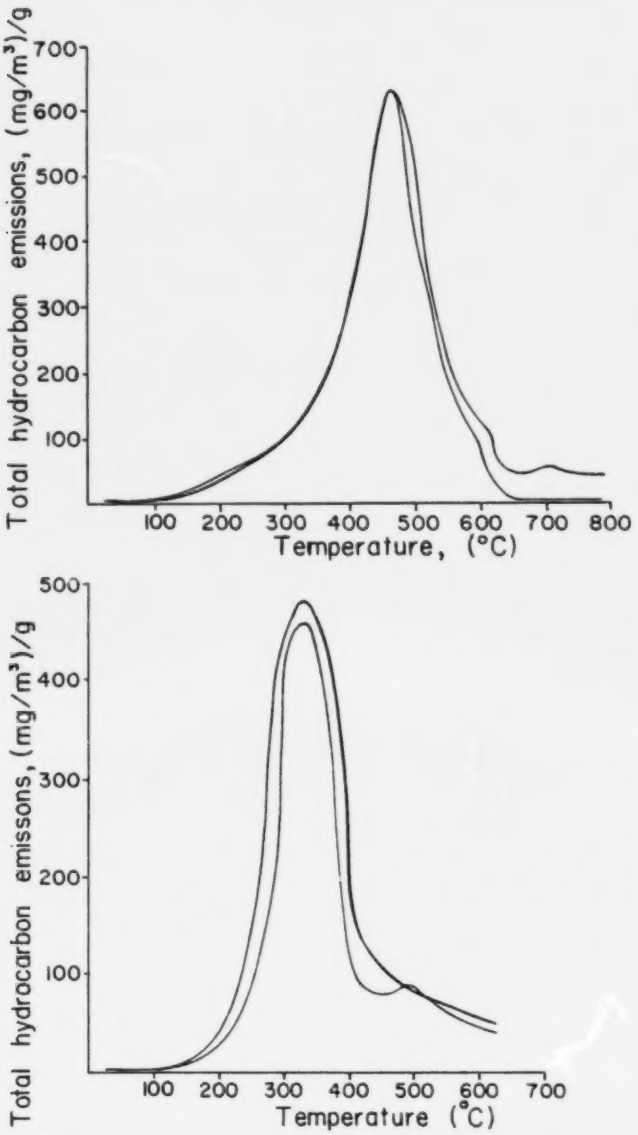


Figure 9. Total Hydrocarbon Emissions. Mill Scale - Plant C.
Top - Heated in Nitrogen. Bottom - Heated in Air.

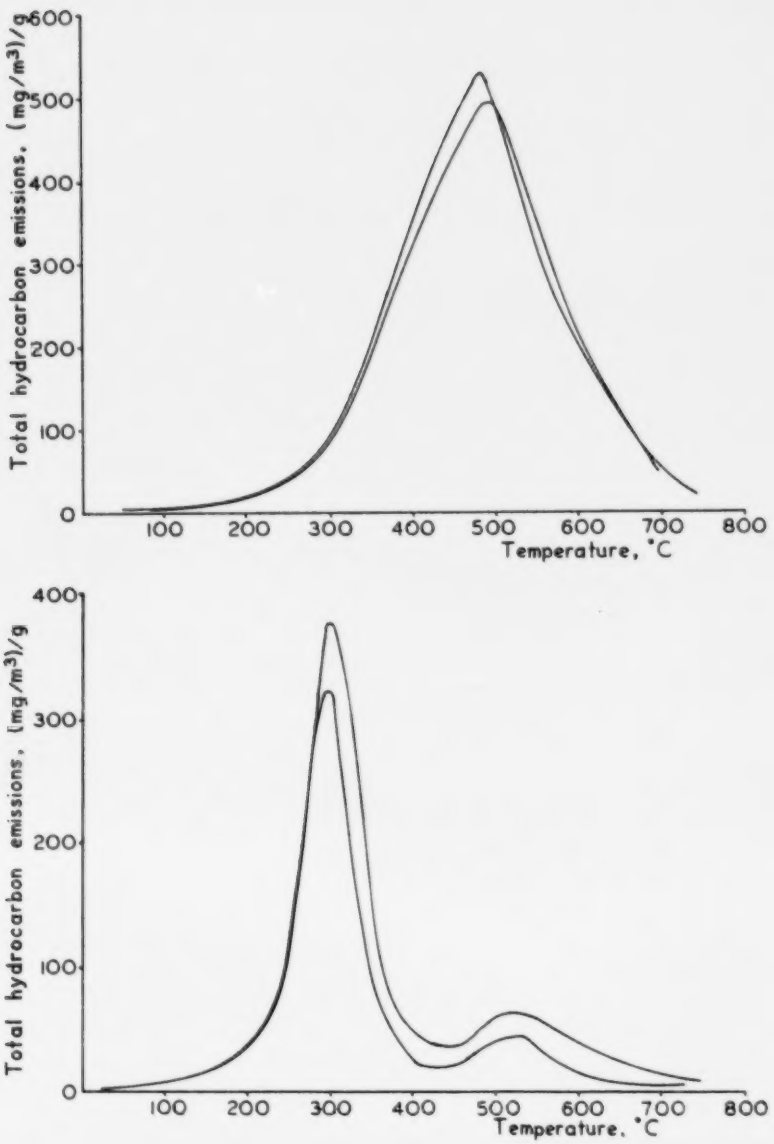


Figure 10. Total Hydrocarbon Emissions. B.F. Flue Dust - Plant A. Top - Heated in Nitrogen. Bottom - Heated in Air.

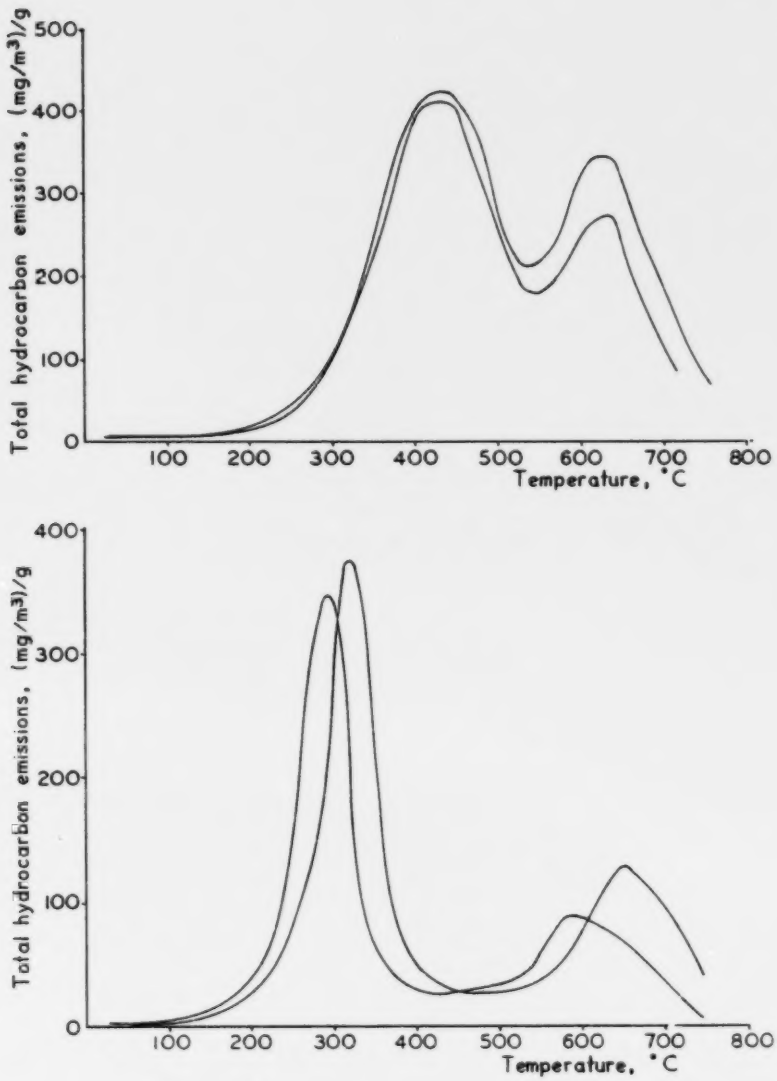


Figure 11. Total Hydrocarbon Emissions. B.F. Flue Dust - Plant B.
Top - Heated in Nitrogen. Bottom - Heated in Air.

No samples of complete sinter mix were obtained from producer's plant C. Samples of the components which go into sinter mix were obtained from all three producers.

Tests were run on all of the sinter mix components received. Only mill scale and blast furnace flue dust were found to be sources of hydrocarbon emissions. Other materials included Mesabi and Venezuela ore fines, Quebec concentrate, calcine, black sand, and anthracite coal.

Figures 7 through 9 show the emissions obtained when mill scale is heated in nitrogen and in air. Again the peaks are lower in air and occur at lower temperatures. Mill scale produces the highest levels of emissions of all the materials tested.

Figures 10 and 11 show the emissions obtained from blast furnace flue dust. Here, too, the peaks are lower in air. In the samples from plant A, the temperatures at which the peak occurs are nearly the same in air and nitrogen. Blast furnace flue dust from plant B shows the same type of double peak as the complete mix from that plant. The rate of emissions at the lower temperature peak is only slightly less in air than in nitrogen, but the higher temperature peak is reduced considerably. Emissions occur from the blast furnace flue dust used by plant B over a very wide range of temperatures.

The results of the full chromatographic analyses on the sinter mixes from plants A and B are shown in Tables 2 and 3. The gas samples were drawn at selected temperatures when samples were heated under conditions duplicating those used for the total hydrocarbon analyses. Values shown are averages of two to six duplicate runs in each case. Results are reported in terms of percent of total hydrocarbons at each retention time. Calibrated retention times for the range of n-paraffins from C1 to C24 are shown in Table 1. This gives an approximate idea of the molecular weight of the species detected at each peak, but since all of the emissions may not be n-paraffins it is approximate only.

Interestingly, these results reveal that the major portion of the hydrocarbon emissions are of very low molecular weight with retention times corresponding to C1 to C4. Since these compounds could not remain in the sinter mix very long, it indicates that considerable thermal decomposition, or cracking, occurs rather than just volatilization.

Furthermore, as the temperature of evolution increases, the emissions become more predominantly in the range of C1 to C2. At the highest temperatures the emissions from plant B's mix are entirely in this range of retention times. This shows, not too surprisingly, that thermal decomposition is greatest at the higher temperatures.

Weight losses on the samples of complete mix generally ran 1 to 2 percent, whether heated in air or in nitrogen, indicating that the fixed carbon which runs about 5 percent did not burn.

Weight gains on the filter generally was less than 0.1% of the sample weight. Hydrocarbon values measured by both the total hydrocarbon and full

Table 2
Chromatographic Analysis of Organic Emissions
from Complete Sinter Mix Used by Plant A

Heated in N_2-100 cc/min

Lower Half Peak* 442°C		Maximum Peak* 496°C		Upper Half Peak* 561°C	
RT(min)**	%	RT(min)	%	RT(min)	%
0.49	3.4				
0.57	1.5				
0.65	21.0	0.66	54.1	0.64	81.5
0.70	10.6	0.73	13.1		
0.85	7.6	0.88	8.9		
1.09	0.9	1.13	0.3		
1.21	3.7	1.25	3.2		
1.45	0.2				
1.59	0.2	1.63	0.05		
1.76	0.2				
1.93	0.5	1.99	0.03		
2.06	0.5	2.11	0.7		
2.71	1.3				
2.87	9.6	2.95	13.0	2.96	3.3
3.67	0.2	3.71	0.3		
4.83	4.3	4.94	2.7		
5.60	0.2	5.71	0.04		
6.84	0.3	6.96	0.1		
7.28	0.3	7.37	0.1		
7.63	0.2				
9.26	0.3				
9.51	0.1				
12.52	1.9	12.62	3.4		
17.45	2.4				
18.45	1.2			18.38	1.6
19.54	5.8			19.68	5.8
19.67	9.9			20.81	0.2
21.09	3.4			21.03	4.2
21.71	7.9			21.71	3.4
23.61	0.3				

*Sampling Temperatures indicated by * on Figure 6 (Top).
**Retention Time Calibrations may be found in Table 1.

Table 2 continued on following page.

Table 2 (Continued)
Chromatographic Analysis of Organic Emissions
from Complete Sinter Mix Used by Plant A

Heated in Air-100 cc/min

Lower Half Peak*** 216°C		Maximum Peak*** 276°C		Upper Half Peak*** 361°C	
RT(min)**	%	RT(min)	%	RT(min)	%
0.55	81.5	0.55	44.9	0.55	76.0
0.64	5.6	0.63	20.7	0.62	16.0
0.77	12.9	0.74	25.3	0.76	6.7
		1.07	6.5		
		2.73	2.6	2.73	1.3

**Retention Time Calibrations may be found in Table 1.
***Sampling Temperatures indicated by * on Figure 6 (Bottom)

Table 3
Chromatographic Analysis of Organic Emissions
from Complete Sinter Mix Used by Plant B

Heated in N_2-100 cc/min

Lower Half First Peak* 430°C		Maximum First Peak* 496°C		Maximum Between Peaks* 560°C		Maximum Second Peak 630°C		Upper Half Second Peak* 685°C	
RT(min)**	%	RT(min)	%	RT(min)	%	RT(min)	%	RT(min)	%
0.65	54.2	0.65	77.8	0.62	99.1	0.63	100	0.63	100
0.72	18.1	0.71	7.6						
0.88	15.5	0.87	7.0						
		1.25	0.8						
3.09	12.1	3.05	6.6	3.05	0.7				
		5.08	trace	5.03	0.2				

Heated in Air-100 cc/min

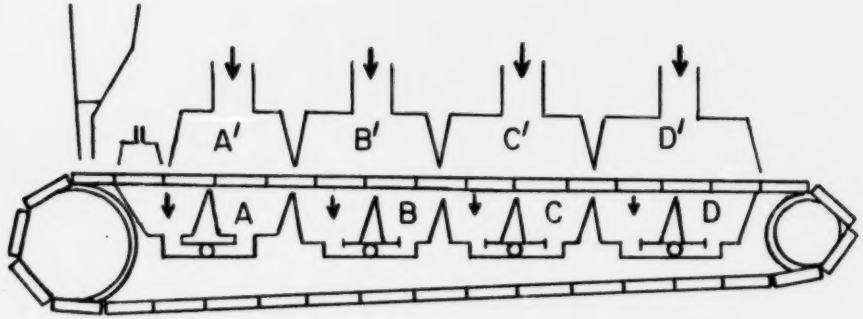
Lower Half First Peak* 197°C		Maximum First Peak* 271°C		Upper Half First Peak* 331°C		Lower Half Second Peak* 457°C		Maximum Second Peak* 532°C	
RT(min)	%	RT(min)	%	RT(min)	%	RT(min)	%	RT(min)	%
0.61	96.1	0.60	77.5	0.61	100	0.61	100	0.61	100
		0.67	6.9						
0.81	3.9	0.82	15.6						

*Sampling Temperatures indicated by * on Figure 6.
**Retention Time Calibrations may be found in Table 1.

chromatographic techniques were not affected by removal of the filter from the line, thus indicating that heavier hydrocarbons were not being filtered out before reaching the analytical unit.

Some of the samples of sinter mix components were subjected to the test procedure two times. During the first test, hydrocarbons were emitted as the specimen was heated to 700°C, as shown in the preceding. When the procedure was run the second time, no detectable hydrocarbons were emitted at any temperature. Furthermore, samples of the sinter mix from producer's plant B were analyzed after the first test run and found to contain 7.5% fixed carbon. This demonstrates that the hydrocarbons can be removed by thermal pretreatment, without eliminating the fixed carbon necessary as fuel.

The relatively high temperatures (up to 800°C in some cases) at which substantial hydrocarbon emissions occur should be of interest to designers of gas recycling systems for sinter lines. Referring to the schematic diagram of a sinter line shown in Figure 12a, most gas recycling plans have proposed to take the gases drawn into the windboxes in the first half of the line (Zones A and B) and recycle them through the hoods over the last half of the line (Zones C' and D'). The temperature profiles in burning sinter beds have previously been shown rather sharply defined (12) as shown in Figure 12b. This indicates that the bottom of the sinter bed would not reach the temperature for maximum emissions of the hydrocarbons until well past the middle of the line. This suggests that the recycling scheme would be improved if the gases from the windboxes in the first quarter of the line (Zone A) were recycled into the hoods on the next quarter (Zone B'), and so on progressively down the line (Zone A to Zone B', Zone B to Zone C', Zone C to Zone D', Zone D' to exhaust). In this way the hydrocarbon would have the chance to be completely burned. Oxygen or make-up air would, of course, have to be added to each zone to keep the oxygen potential high enough. This technique would also minimize the quantity of gas to be treated in the particulate control system.



SINTER LINE RECYCLING SCHEMES

USUAL: WINDBOXES A AND B FEED
HOODS C' AND D'

PROPOSED: WINDBOX A FEEDS HOOD B'
WINDBOX B FEEDS HOOD C'
WINDBOX C FEEDS HOOD D'

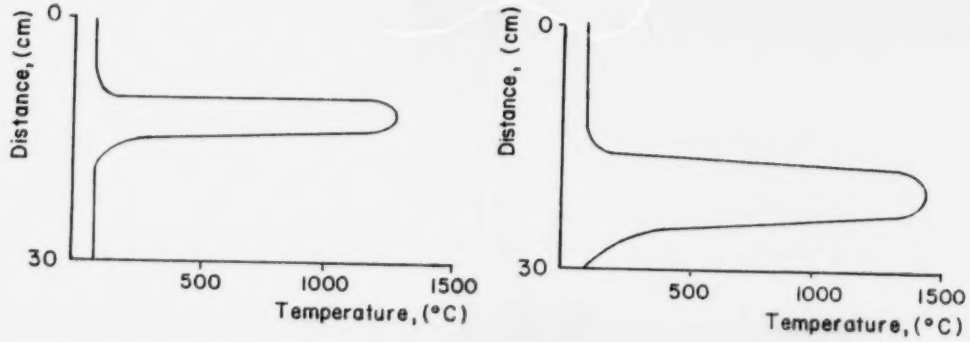


Figure 12a. (Top) Diagram of an iron ore sinter line showing schemes for recycling gases to obtain complete burning.

Figure 12b. (Bottom) Temperature profiles in sinter beds as a function of position of flame front relative to distance from top of bed.

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